

EXPERIMENTAL EVALUATION AND NUMERICAL SIMULATIONS OF NANO-MATERIALS IN INFRASTRUCTURE FIRE APPLICATIONS

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ABSTRACT

Although the coating masonry walls with polymeric elastomers can mitigate the effects of projectile strike in blast or explosion, it may also increase the fire hazard to the structure and the occupants. While a rigorous assessment of this problem would require full scale fire tests, considerable insights can be gained by performing bench scale tests in conjunction with computer simulations. A joint experimental/numerical program is presented in this paper to evaluate the extent to which blast-resistant coating applied on masonry walls may contribute to the growth of an existing fire. The experimental data were obtained by performing cone calorimeter HRR measurements. Flammability characterization and heat flux generated for structural systems and components, coated with blast-resistant and fire-retardant polymeric coatings, were performed using the NIST Fire Dynamic Simulator (FDS). In these simulations, structural concrete columns and masonry walls were exposed to an existing fire. A coupled thermal/structural finite element analysis was then performed using ANSYS to assess the structural integration fire effect.

1. INTRODUCTION

The development of a blast-resistant coating for structural members with good fire performance will provide buildings with multi-hazard protection against explosions and fire following a blast event. It is desirable to have coatings which possess a thermal barrier to heat, in such that the temperature of structural elements can remain below the critical temperature for as long as possible. Since most of materials considered for blast-resistant coatings are polymer-based and are flammable, employing them may create an unacceptable fire hazard. The purpose of this paper is to identify coating materials that provide the best compromise between blast protection and fire safety.

An important consideration of building fire safety is the flammability characteristics of the interior walls, columns and ceilings finishing, especially if they are coated with polymeric materials. The interior wall finishing represents a large surface area over which flame can spread. Such flame can change a small fire into a room flashover [1]. If the burning duration of a surface element is longer than the ignition time of a neighboring element, flame spread will occur. If not, then a local burnout is expected [2]. Flame spread has been modeled theoretically [2-5]. The existing models are mainly concerned about the critical nature of the flame spread, specifically for thin combustible layers coated on noncombustible substrates.

Fire growth as a function of time is a safety concern. Cleary [6] first formulated a theoretical model of fire growth output as a function of time, in terms of material properties and orientations for flat surfaces in application to floors, walls and ceilings. Quintiere [2] developed a mathematical model to simulate fire growth on the wall and ceiling materials when subjected to a room-corner fire test exposure. The model predicts the area of burning, the upper layer gas temperature and the rate of energy release as a function of time.

Parasad et al. [7] conducted coupled simulations of fire dynamics and thermal response of World Trade Center (WTC) towers. A radiative heat transfer model was used to couple the gas phase energy release and transport phenomena to the stresses on the load-bearing members. The radiative transport equations are employed in solving for the heat flux as a function of

temperature, hot layer depth, soot concentration and orientation of the structures. These outputs are imported into finite element codes for time-independent, three-dimensional structural analysis. The finite element analysis (FEA) uses these results to account for thermal material strength degradation and its effect on elastic -plastic stress-strain relationships.

Brown et al. (1988) [8] evaluated the fire performance and flammability of composite materials by cone calorimeter measurements, to assist the Navy in its selection criteria for ship components. The materials investigated by Brown et al. were mainly polymer resins reinforced with fiber glass fabric. McGraw and Mowrer (1999) [9] conducted cone Calorimeter flammability measurements for painted gypsum wallboards. Experiments for eight coats of latex paint over one coat of primer were run at heat fluxes between 25 kW/m^2 - 75 kW/m^2 .

It is known that the fire performance of polymeric materials may be enhanced by adding inorganic nanoadditives and fire-retardants. For example, Wang et al. investigated the flammability characteristics and fire retardancy of polymeric-clay nanocomposites [10]. Polymers included in their study were: polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polypropylene (PP), ethylene-vinyl acetate (EVA), epoxy resins, PMMA, poly (vinyl chloride) (PVC), polyamides (PA) and others. Polymeric-clay nanocomposites were shown to reduce flammability and exhibited improved mechanical properties. They also proposed mechanisms by which the nanocomposites enhance the thermal and fire stability of polymers. Gilman et al. [11], studied the flammability properties of polymer-layered silicate polypropylene/polystyrene nanocomposites. They reported reductions in flammability by the addition of delaminated montmorillonite (MMT) clay.

After surveying current literature, we observed that limited work has been reported on the fire behavior of thin combustible polymeric layers coated on noncombustible substrates such as concrete. Coated concrete-structural elements are the most commonly used building materials in the USA. It is vital to perform fire performance characterizations to evaluate their safety in different structural system models. In this paper, we report on measurements of the heat release rates (HRRs) of polymeric nanocomposite plaques and polymeric nanocomposite coated concrete blocks. The fire performance of structural components and structural systems is investigated by performing simulations using the NIST Fire Dynamic Simulator (FDS). Coupled

thermal/structural finite element analysis is adapted to determine the maximum stresses and displacements in the different structural components.

2. PROCEDURE

MATERIALS

Two types of materials were investigated in this paper: The first type is comprised of experimental blast-resistant polymers based on an elastomer polymer (polyurea) and a thermoset polymer (epoxy). These polymers were reinforced with nanoadditives including exfoliated graphene nanoplatelets and polyhedral oligomeric silsesquioxane (POSS). The second type of material was comprised of commercial fire resistant formulations. A detailed description for the material fabricated is summarized in the following sections:

i. BLAST-RESISTANT MATERIALS

The flexible epoxy used is made of 100phr Epon 828/50phr Jeffamine D-400/25phr Jeffamine D-2000. Polyurea LINE-X XS-350 used is a two-component polyurea supplied by Protective Coating Inc. Polyurea is mixed with Polyhedral Oligomeric Silsesquioxane (POSS). POSS used is a class of silicon based nanochemicals designed to fulfill various mechanical functions supplied by Hybrid Plastics Inc. Epoxy reinforced with exfoliated graphene nanoplatelets is produced at Michigan State University (Composite Materials & Structures Center). Exfoliated graphene nanoplatelets-15 is made from Asbury 3772 using High Power Microwave. Prior to use, exfoliated graphene nanoplatelets are kitchen-microwaved for 1 min/ 10-15g. Finally polyurea is reinforced with exfoliated graphene nanoplatelets.

ii. FIRE-RETARDANT MATERIALS

LR, Tyfo®, is a liquid (ethylene propylene) rubber coating used supplied from Fyfe Inc. LR HP, Tyfo®HP is a two-component epoxy fire retardant-intumescent

coating used based on non-halogenated phosphates. LR FC F, Tyfo®FC F used is a two-part epoxy coating system specially formulated to provide an increase in existing fire rating. Tyfo® F is a single component formulation designed to be applied over Tyfo® FC. The Tyfo® FC F system provides an increase to the fire rating of an element as per ASTM E-119 (2-hours wall rating) and provides a class 1, ASTM E-84 flame and smoke rating. Type 4 Tyfo® Blast-Flex Type 4 used a two-component polyurea based system with fire-resistance additive. The fire protection material is supplied by Fyfe Inc.

STATE EXAMINATION OF FIRE

i. EXPERIMENTAL MEASUREMENTS (CONE CALORIMETER)

Cone calorimeter HRR measurements were made on a number of blast-resistant and fire-retardant coating materials on a FTT dual cone calorimeter. The samples were exposed to incident heat fluxes of 30, 40, 50 kW/m² with an exhaust flow of 24 L/s using the standardized test procedure (ASTM E-1354-07) with some modifications as described below.

All samples were tested without frame and grid, but the solid coating samples (polyurea, epoxy, and LR on cinder block) were tested in a shallow thick-walled aluminum dish to capture any dripping. The coated cinder block samples were wrapped with aluminum foil on the back side of the sample only to form a small pan that would capture any dripping off the sample surface during burning. The aluminum foil was not wrapped snugly around the sample so that any dripping behavior could be clearly observed.

ii. NUMERICAL SIMULATIONS (FIRE DYNAMIC SIMULATOR)

FDS is computer software which solves the equations that describe the thermal decomposition of the solid and the gas phase mixing, transport and combustion of

the resulting fuel [12]. Smokeview is companion software that images and animates the FDS output files [13].

Heat release rate (HRR) is an important property of materials that determines whether there is sufficient thermal energy for fire growth and spread. In addition to HRR, several other reaction properties are used to characterize the fire behavior of composites. These include flame spread, smoke formation and CO emission [14].

A series of heat release rate simulations for the following blast-resistant and fire-retardant materials were conducted using the NIST Fire Dynamic Simulator (FDS): polymeric coated blocks (Polyurea, Polyurea + POSS, Polyurea + 6% graphene, Epoxy, Epoxy + 6% graphene, LR, LRFCF, LRHP and Type 4. The objective of this work is to calculate the time evolution function of the heat flux (Q) temperature (T), (Q(t), T(t)), and to compare the flammability of the different polymeric blast-resistant and fire-retardant materials.

- *Single Room Fire Model*

FDS simulations were performed to determine the extent to which various candidate materials contributed to a fire confined to an office space (6m x 3m x 3m high) in a building. The office space has three walls and is open in front. The (533 /pm 50 kW) fire was located near the back wall, which is specified by assigning thermo-physical properties consistent with a 3mm coating of the candidate material on concrete. The floor and ceiling were assigned properties typical of gypsum, while the front of the space is left open to the air.

- *Concrete Column Model*

Representative concrete columns were included in the FDS and FEA simulations. The following geometry dimensions were used: a cross section of (18"x18"=45.72cmx45.72cm), height of (3) m with a 3 mm

polymeric coating applied to its surface. Solid phase thermocouple devices were placed on the front side of the column (near fire), to measure the temperatures and heat fluxes on the surfaces of the coated columns during the simulations, at the following intervals: (0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 2.5, 2.6, 2.7, 2.8, and 2.9) m. A demonstration is shown in Figure 1. The simulations were run for 200 s with a time step of 1 s.

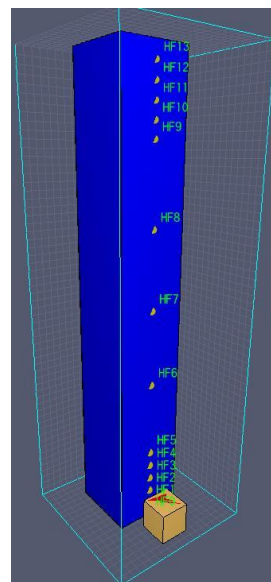


Figure1: Coated Concrete Column FDS Setup

- Masonry Wall Model

Typical masonry walls of dimensions (3mx3mx0.20m) and (3) mm coating thickness were assembled for FDS numerical simulations. Each masonry wall configuration was simulated for 200 sec at a time step of 1 sec as a part of the single room structural system. As was done for the columns, solid phase thermocouple devices were placed on the front side of the masonry walls (near fire) at intervals (0, 0.1,

0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 2.5, 2.6, 2.7, 2.8, and 2.9) m, to measure the heat fluxes and wall temperatures during the simulation.

STRUCTURAL INTEGRITY (FINITE ELEMENT ANALYSIS)

Coupled thermal/structural finite element analysis using ANSYS [15] was adapted to determine the maximum stresses and displacements in the different structural components.

The objective was to determine the effect of fire on different structural elements integrity to predict the failure. Spatial and temporal variation in temperature will result in thermally induced stresses/strains and reduce load bearing capacity that could lead to failure of the structural element. The peak heat flux $Q(t)$, measured using the thermocouple devices in the FDS simulations, was applied to the concrete columns and the masonry walls. This step was followed by a thermal transient finite element simulation to calculate the nodal temperature distribution corresponding to the applied peak heat flux $Q(t)$. Finally, the nodal temperature distribution generated from the thermal finite element analysis was applied to solve for the stresses/strains developed in the structural elements.

3. RESULTS AND DISCUSSION

EXPERIMENTAL MEASUREMENTS (CONE CALORIMETER)

Time dependent HRR curves obtained from cone calorimeter measurements on polyurea-POSS and epoxy-exfoliated graphene nanoplatelets plaques (~1.0 cm thick), are displayed in Figure 2. The HRR plateau occurring during the initial stages of the burn is indicative of quasi-steady burning that is characterized by a thin, well-defined pyrolysis zone and constant temperature gradient throughout the sample. This was followed by a dramatic increase in HRR as more and more of the sample thickness became involved in pyrolysis. The burning behavior of the epoxy plaques was particularly violent as flaming shards were observed to shoot out from the top and

sides of the burning plaque. The presence of the graphene additive did, however, appear to mitigate this effect.

The time dependent HRR plots obtained from cone calorimeter measurements for the polymer-coated cinder blocks are shown in Figure 3.

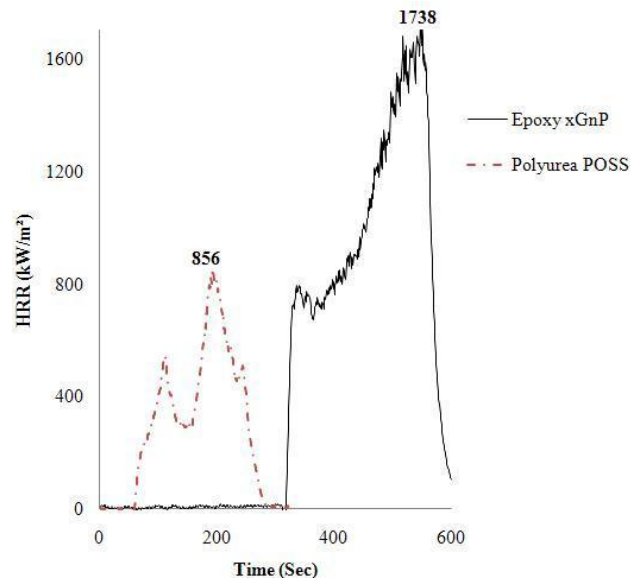
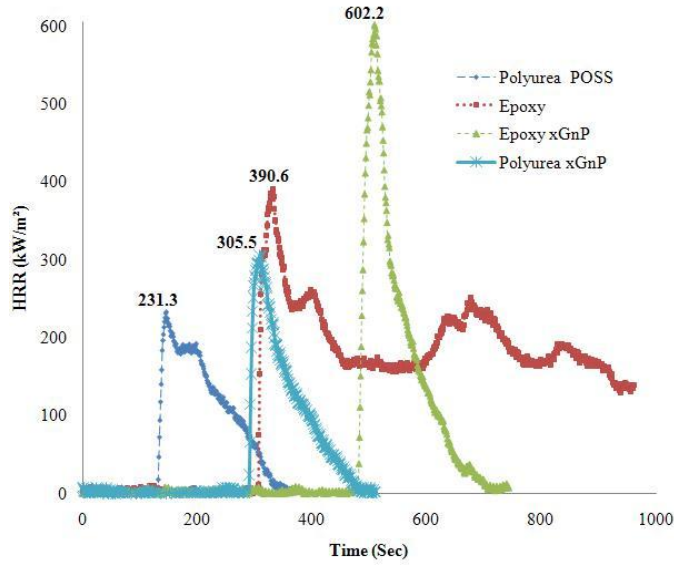
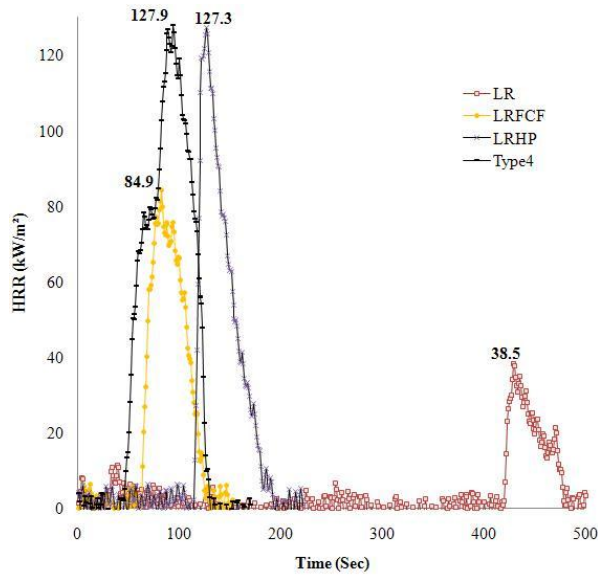


Figure2: Time Dependent HRRs Obtained From Cone Calorimeter Measurements for Polymer Plaques



(a) Blast-Resistant Materials



(b) Fire-Retardant Materials

Figure3: Time Dependent HRRs Obtained From Cone Calorimeter Measurements for Coated Cinder Blocks

Although the peak HRRs (PHRRs) for the polymer plaques are quite high approaching 2000 kW/m², the HRRs from the polymer coated cylinder blocks were much more modest as indicated in Figures 4 and 5. Furthermore, as revealed by

Figure 5, the presence of the cinder blocks effectively eliminates the strong dependency of HRR on incident heat flux that was observed for the corresponding polymer plaques. This justification will simplify the simulation performance of a single HRR value (rather than a function that describes the dependence of HRR on incident flux) for each simulated candidate material.

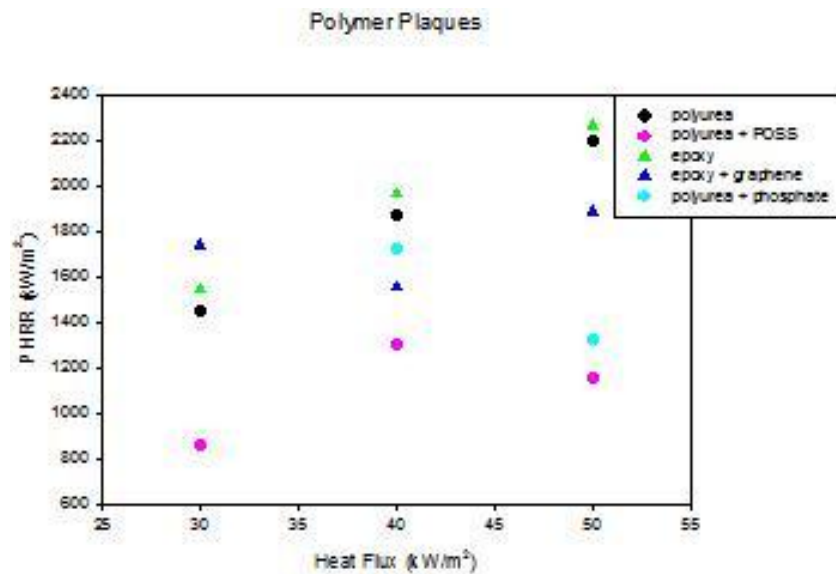


Figure4: HRR Measurements for Polymer Plaques

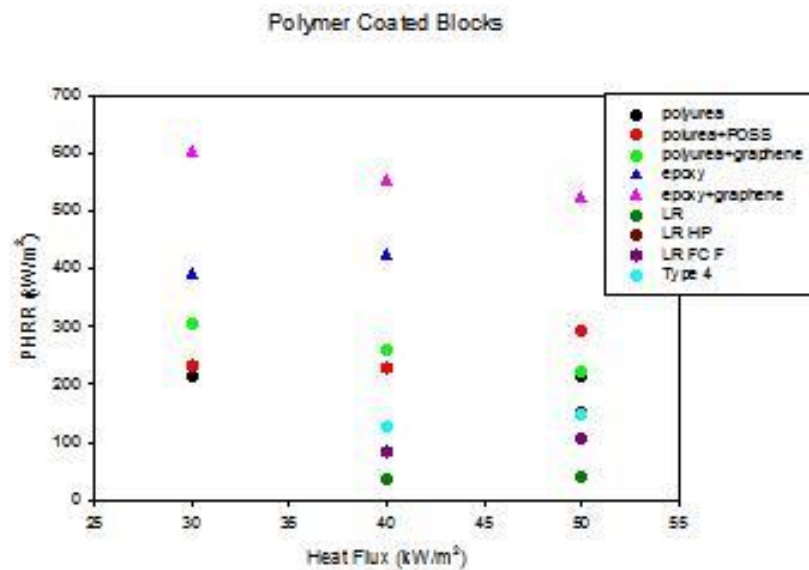


Figure5: HRR Measurements for Coated Cinder Blocks

The data listed in Table I indicate that while the presence of the additives (POSS, phosphate, graphene) tends to reduce the HRRs of the polymer plaques, they do not seem to provide much benefit when these materials are used as coatings on cinder blocks. Indeed, the presence of graphene appears to increase the HRR of the epoxy coating significantly.

The results obtained from the cone calorimeter tests indicate that the fire performance of the commercial LR fire retardant was far better than any of the other coatings examined in this study. During the tests on the LR coated blocks, it was observed that the flames were confined to a small fraction of the surface.

Table I: PHHRs for Candidate Material

Material	Incident Flux (30 kW/m ²)	Incident Flux (40 kW/m ²)	Incident Flux (50 kW/m ²)
Polymeric Plaques			
Polyurea	1450	1875	2201
Polyurea Phosphate	n.a.	1720	1327
Polyurea POSS	856	1299	1156
Epoxy	1544	1966	2263
Epoxy Graphene	1738	1553	1887
Polymeric coated cinder blocks			
Polyurea	213	260	216
Polyurea POSS	233	229	293
Polyurea Graphene	305	261	221
Epoxy	391	422	n.a.
Epoxy Graphene	602	552	552
LR	---	38	39
LR HP	---	127	152

Material	Incident Flux (30 kW/m ²)	Incident Flux (40 kW/m ²)	Incident Flux (50 kW/m ²)
LR FC F	---	84	108
Type 4	---	128	147

The polyurea appears to perform better than the epoxy, which has higher PHRRs, drips, and spalls, burning pieces of the epoxy flew off the blocks during the experiments. The presence of the graphene mitigates the dripping and spalling observed in the pure epoxy coated bricks and generally prolongs ignition times. Unfortunately, the graphene also appears to increase PHRR at low thermal flux. The longer ignition times and higher PHRRs may be due to an increase in thermal conductivity imparted by the graphene.

NUMERICAL SIMULATIONS (FIRE DYNAMIC SIMULATOR)

i. SINGLE ROOM FIRE MODEL

Snapshots of the heat release rate per unit volume (HRRPUV) from the simulations generated by FDS are shown for the various coatings in Figure 6.

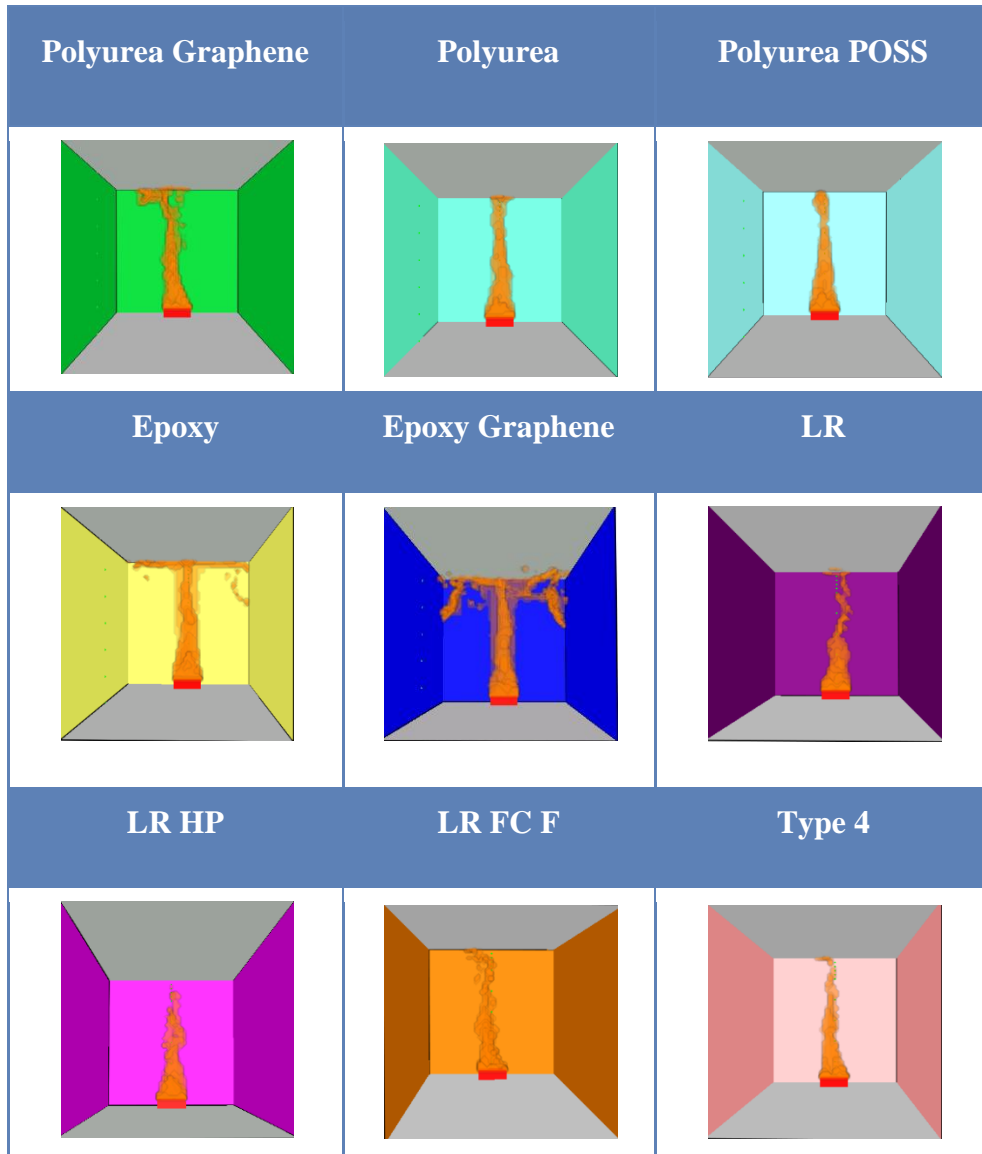


Figure6: HRRPUV for Coated Masonry Walls in a Single Room Model
Snap Shots

The blast-resistant and the fire-retardant coatings are distinguished by assigning the average values of the HRRs (per unit area) measured in the cone calorimeter tests. The coatings were programmed to ignite when the surface temperature exceeded 350 C°. The maximum HRR of the room fire simulated for the coating material candidates and the control (bare concrete) are listed in Table II.

These data indicate that the LR and Type 4 fire retardant coatings are very effective in reducing the HRR from the polymer coated walls. The effect of the addition of POSS and graphene to the polyurea and epoxy coatings is either minimal or, in the case of the epoxy, least.

Table II: Concrete Coated Blocks Maximum HRR of Simulated Fires

Coating Material	Max HRR (kW/m ²)
No Coating	593
Polyurea	850
Polyurea POSS	827
Polyurea Graphene	829
Epoxy	1120
Epoxy Graphene	1520
LR	605
LRFCF	586
LRHP	621
Type4	608

Fire smoke is a mixture of small fragments of fiber and ultra fine carbon particles (soot). The amount of smoke produced when a composite material burns is a concern because smoke obscures visibility thereby making it difficult for occupants to escape from the fire. Thus, if all other factors are equal, materials that produce a lot of smoke when they are burned are less safe than materials that produce less smoke. Figure 7 shows smoke snapshots at 100 sec for the room FDS model.

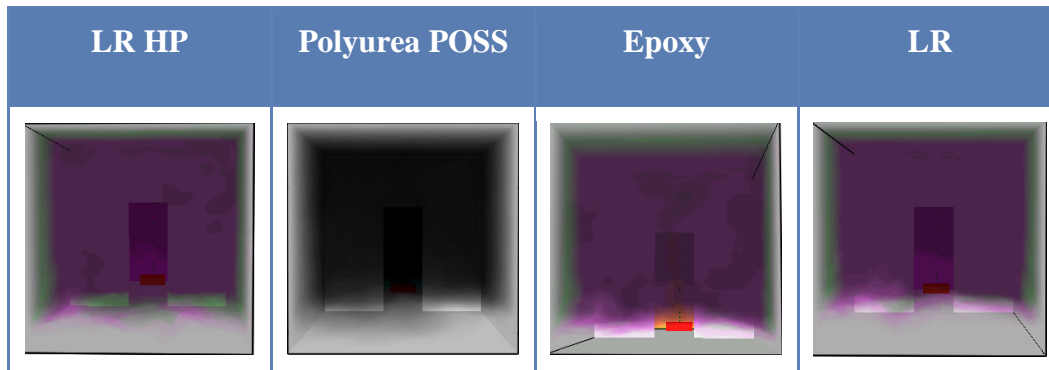


Figure7: Smoke for Coated Walls in a Multiple Room Mode Snap Shots

ii. CONCRETE COLUMN MODEL

Figure 8 demonstrates the heat release rate per unit volume (HRRPUV) snapshots for the different simulated coated columns. From Figure 8, it appears that the flame spread is the least for the polyurea POSS and the greatest for the epoxy graphene coated columns. Figure 9 shows the maximum values of the heat flux plots as a function of time. Table III summarize the maximum heat flux captured by the solid phase devices described above. Not surprisingly, the results in Table III confirm that the polymeric coatings have increased the heat transfer per unit area compared to the uncoated and gypsum covered concrete columns which do not contribute to the HRR. We note further that the gypsum covering is very effective in insulating the concrete columns from the heat generated by the existing fire.

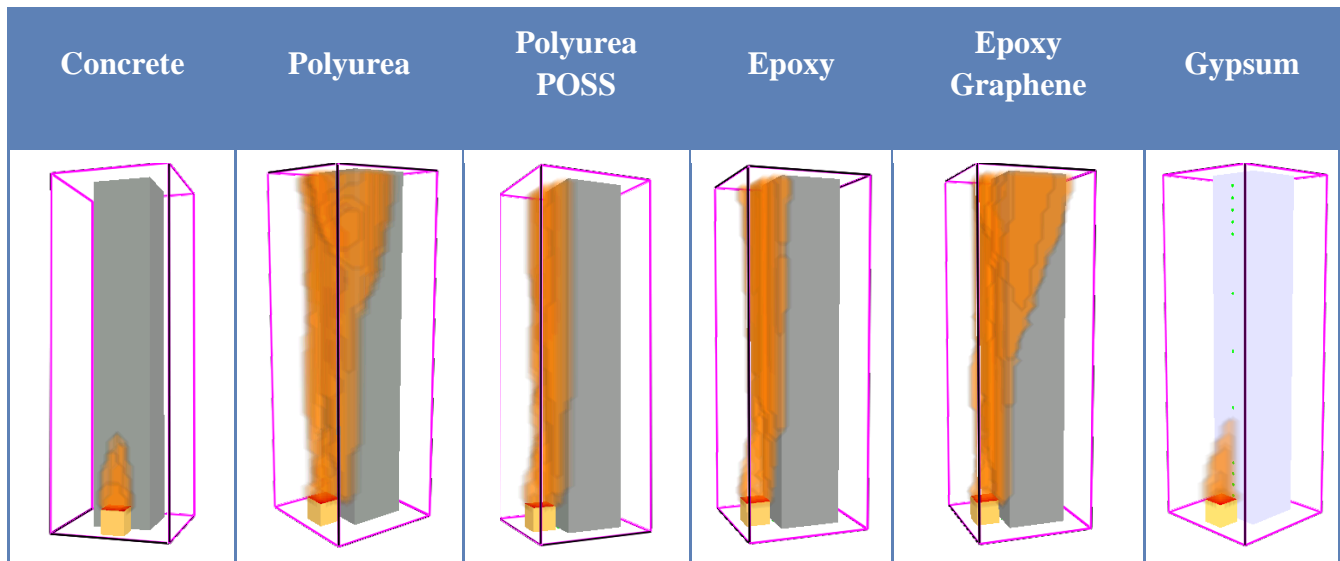


Figure8: HRRPUV for Coated Concrete Columns FDS Snap Shots

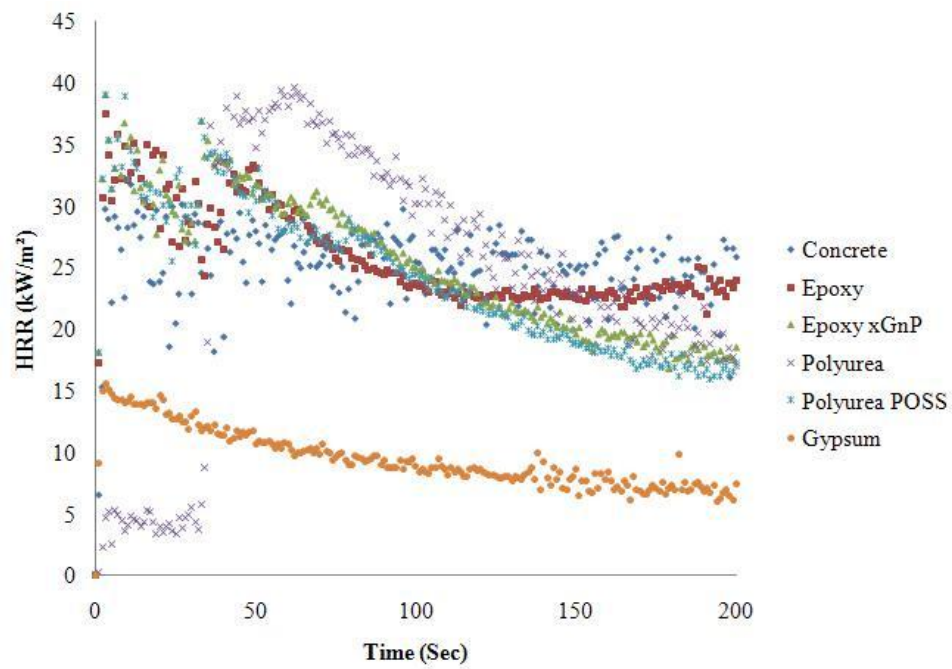


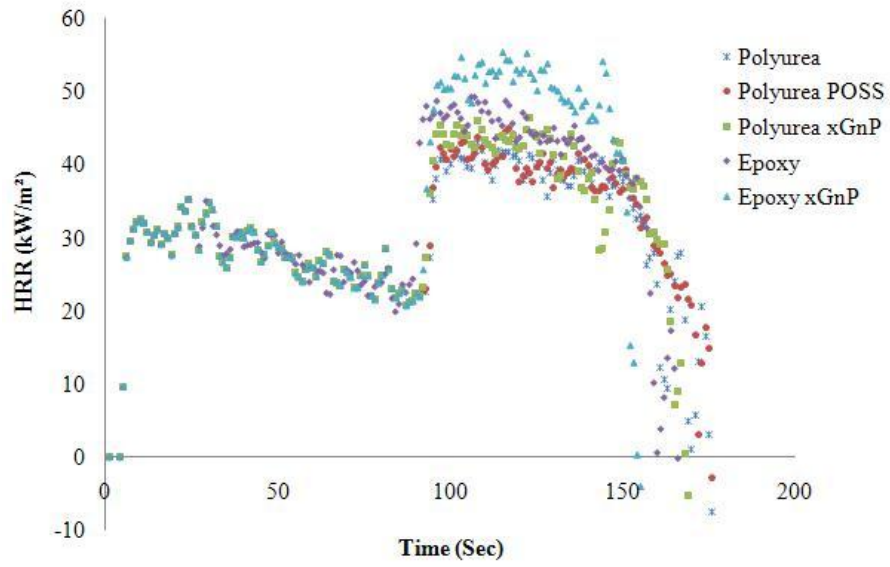
Figure9: Q(t) Plots for the Concrete Columns

Table III: Maximum Q(t) Coated Concrete Columns Simulations (kW/m²)

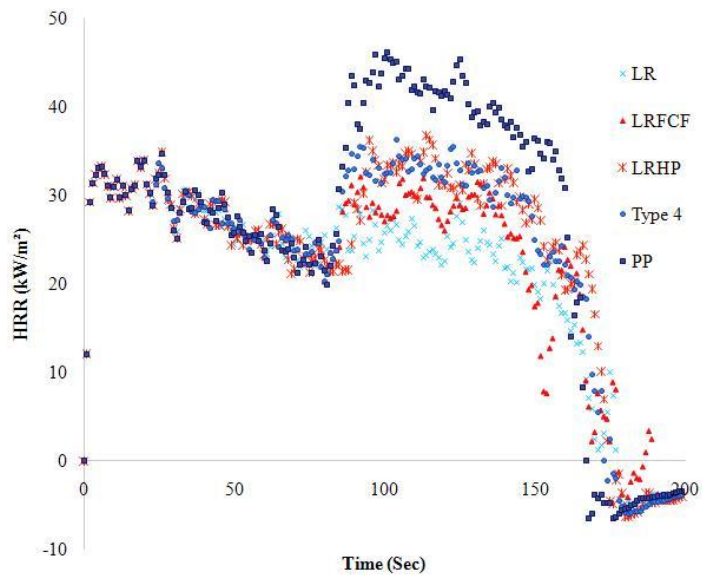
Device Height (m)	Concrete	Polyurea	Polyurea POSS	Epoxy	Epoxy Graphene	Gypsum
0	0.485	0.436	0.425	0.40	0.386	1.16
0.1	2.173	1.972	1.963	1.86	1.761	3.07
0.2	35.234	28.727	29.017	29.85	25.687	11.93
0.3	38.201	36.123	36.263	33.61	36.912	13.38
0.4	34.775	39.752	39.226	31.43	39.515	12.68
0.5	28.578	39.710	37.062	26.71	37.611	11.37
1	4.501	8.754	6.807	5.85	5.412	2.19
1.5	2.066	3.054	2.737	2.74	0.756	0.71
2	1.304	2.106	1.987	1.66	0.391	0.55
2.5	1.083	1.632	1.536	1.35	0.339	0.64
2.6	0.956	1.496	1.381	1.31	0.325	0.59
2.7	0.841	1.355	1.240	1.25	0.316	0.53
2.8	0.754	1.219	1.122	1.20	0.313	0.47
2.9	0.738	1.108	1.013	1.18	0.309	0.42

iii. MASONRY WALL MODEL

Figure 10 demonstrates the heat flux $Q(t)$ evolution for the coated masonry walls. Figure 11 indicates that the addition of POSS to polyurea tends to lower the monitored surface temperature. Table IV below summarizes the maximum heat flux captured by the solid phase devices at mentioned heights. However, LR has shown the minimum released heat fluxes and surface temperatures.



(a) Blast-Resistant Materials



(b) Fire-Retardant Materials

Figure10: Maximum Heat Flux at (0.5m) Profiles Masonry Wall Simulation (kW/m²)

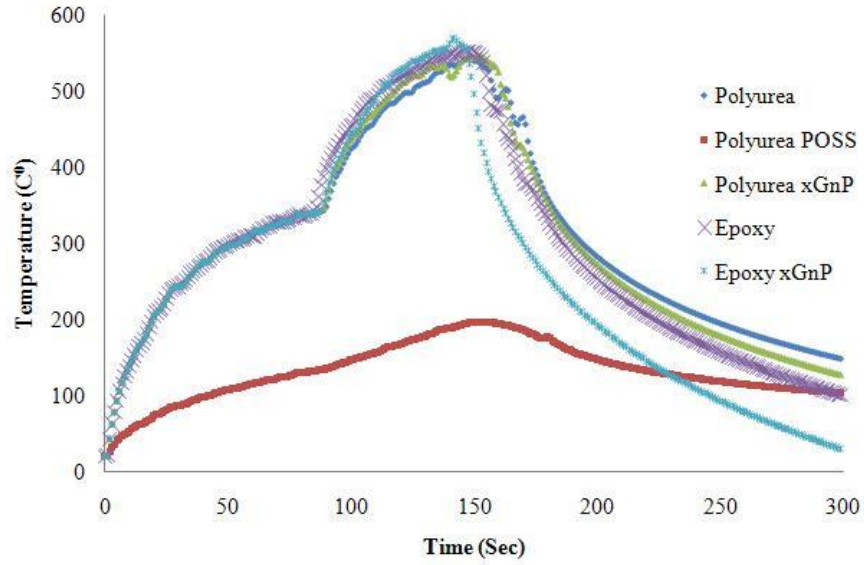


Figure11: Maximum T(t) Profiles Masonry Wall Simulation (kW/m^2)

Table IV: Maximum Q(T) Coated Masonry Walls Simulation (kW/m^2)

Device Height (m)	Polyurea	Polyurea POSS	Polyurea Graphene	Epoxy	Epoxy Graphene	LR	LR HP	LR FC F	Type 4
0	11.93	11.1	13.0	13.4	13.0	9.8	10.5	9.7	9.8
0.1	14.70	13.4	---	---	---	13.0	12.8	13.0	12.1
0.2	31.97	24.0	---	---	---	26.7	22.7	27.4	22.5
0.3	40.79	24.7	---	---	---	29.7	30.1	30.6	29.8
0.4	46.34	37.5	---	---	---	32.8	36.8	34.0	33.6
0.5	48.59	45.1	46.3	51.7	56.1	33.1	39.4	34.3	34.5
1	51.15	47.3	51.1	59.9	61.3	27.0	37.6	27.5	30.5
1.5	46.52	49.5	51.8	59.9	66.0	17.2	23.8	17.4	15.8
2	28.50	45.0	50.7	59.9	65.6	11.1	19.7	10.0	13.5
2.5	18.93	22.9	52.3	62.5	63.4	8.4	16.6	8.1	15.2
2.6	18.29	17.7	---	---	---	8.3	17.2	8.0	15.8
2.7	17.33	17.2	---	---	---	8.2	17.6	7.9	17.4
2.8	16.80	16.2	---	---	---	8.1	17.7	7.8	17.7
2.9	15.94	15.8	---	---	---	8.2	18.4	7.4	17.9

FINITE ELEMENT SIMULATIONS

i. CONCRETE COLUMN MODEL

To analyze the effect of the fires on the structural elements and to predict the failure, subsequent concrete columns were loaded with the temperature data obtained from the finite element thermal analysis. Spatial and temporal variation in temperature distribution results in thermally induced stresses/strains and reduced bearing capacity. A typical nodal temperature distribution for a concrete column is demonstrated in Figure 12.

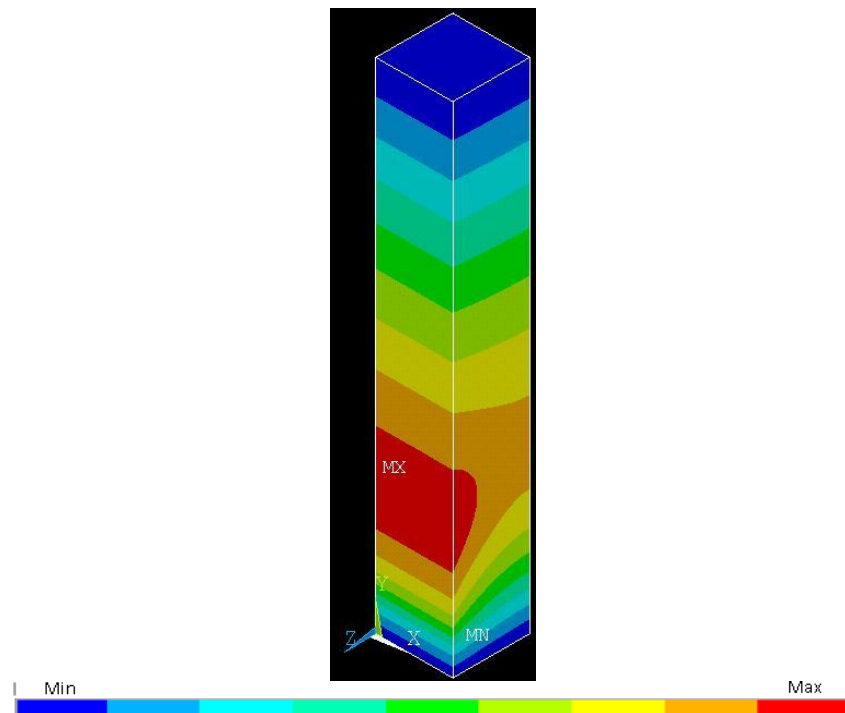
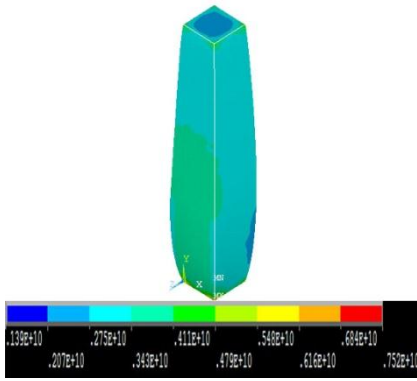
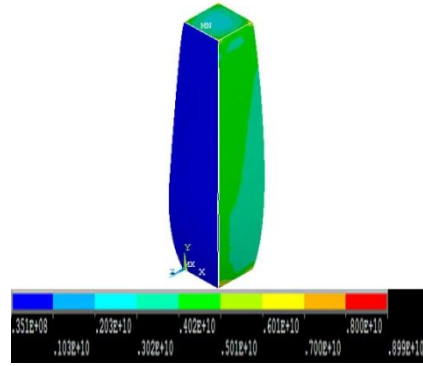


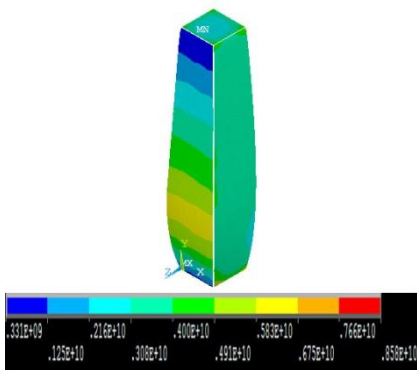
Figure12: Nodal Temperature Distribution in Concrete Coated Columns



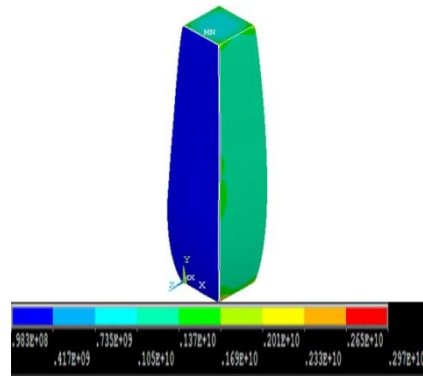
(a) Bare Concrete



(b) Polyurea POSS

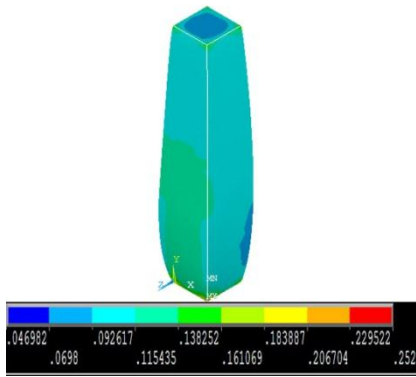


(c) Epoxy

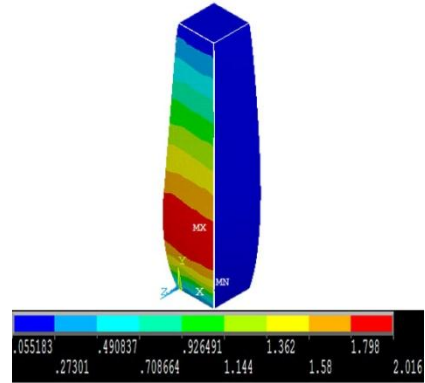


(d) Gypsum

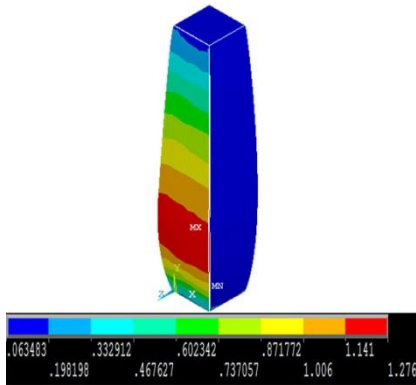
Figure13: Von Mises Stress (Pa) Nodal Distribution in Concrete Coated Columns



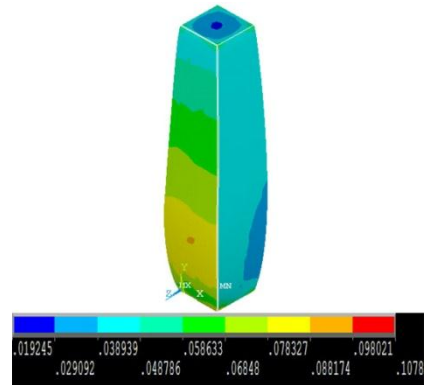
(a) Bare Concrete



(c) Epoxy



(b) Polyurea POSS



(d) Gypsum

Figure14: Von Mises Strain Nodal Distribution in Concrete Coated Columns

A time dependent thermal nodal analysis was adapted to calculate the temperature nodal distribution and to reveal the thermal response of the concrete columns that can potentially result in structural failure. The von Mises stresses/strains are shown Figures 13 and 14. The polyurea based nanocomposites performed better than the epoxy based in term of maximum stresses/strains.

ii. MASONRY WALL MODEL

The fire effect of polymer reinforced composites coated masonry walls was studied using ANSYS coupled thermal/structural analysis. The maximum/minimum stresses/strains are obtained for the coated masonry walls with the blast-resistant and fire-retardant coatings. The masonry walls are exposed to the heat fluxes per unit area collected from solid phase devices installed on the front side of the masonry wall from the FDS simulations. A time dependent thermal nodal analysis was conducted to calculate the temperature nodal distribution and to reveal the thermal response of the masonry walls. A typical nodal temperature distribution is shown in Figure 15.

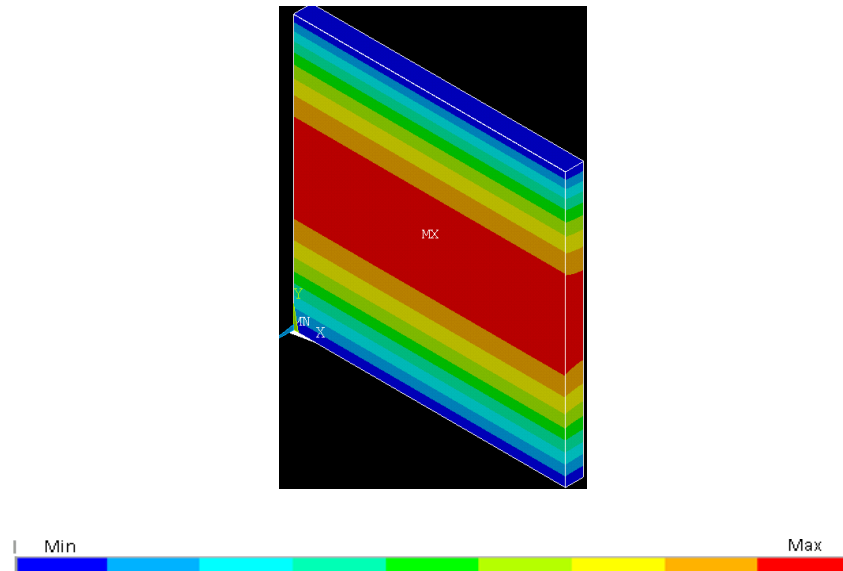
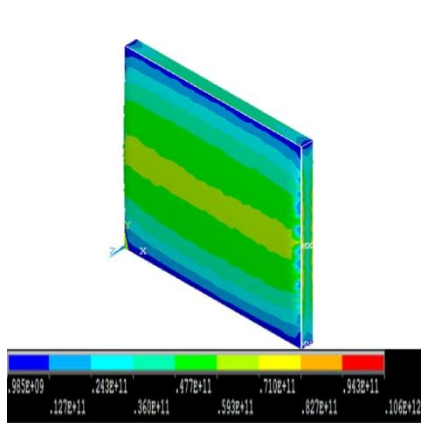
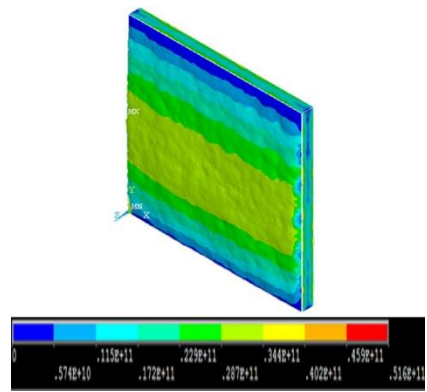


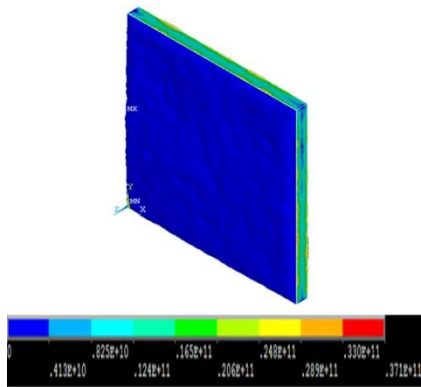
Figure15: Nodal Temperature Distribution in Masonry Coated Walls



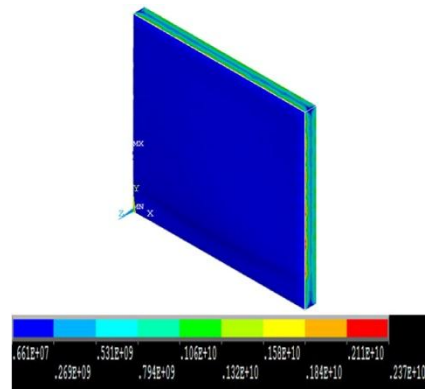
(a) Epoxy



(b) LRHP



(c) LR



(d) Polyurea POSS

Figure16: Von Mises Stress (Pa) Nodal Distribution in Masonry Coated Walls

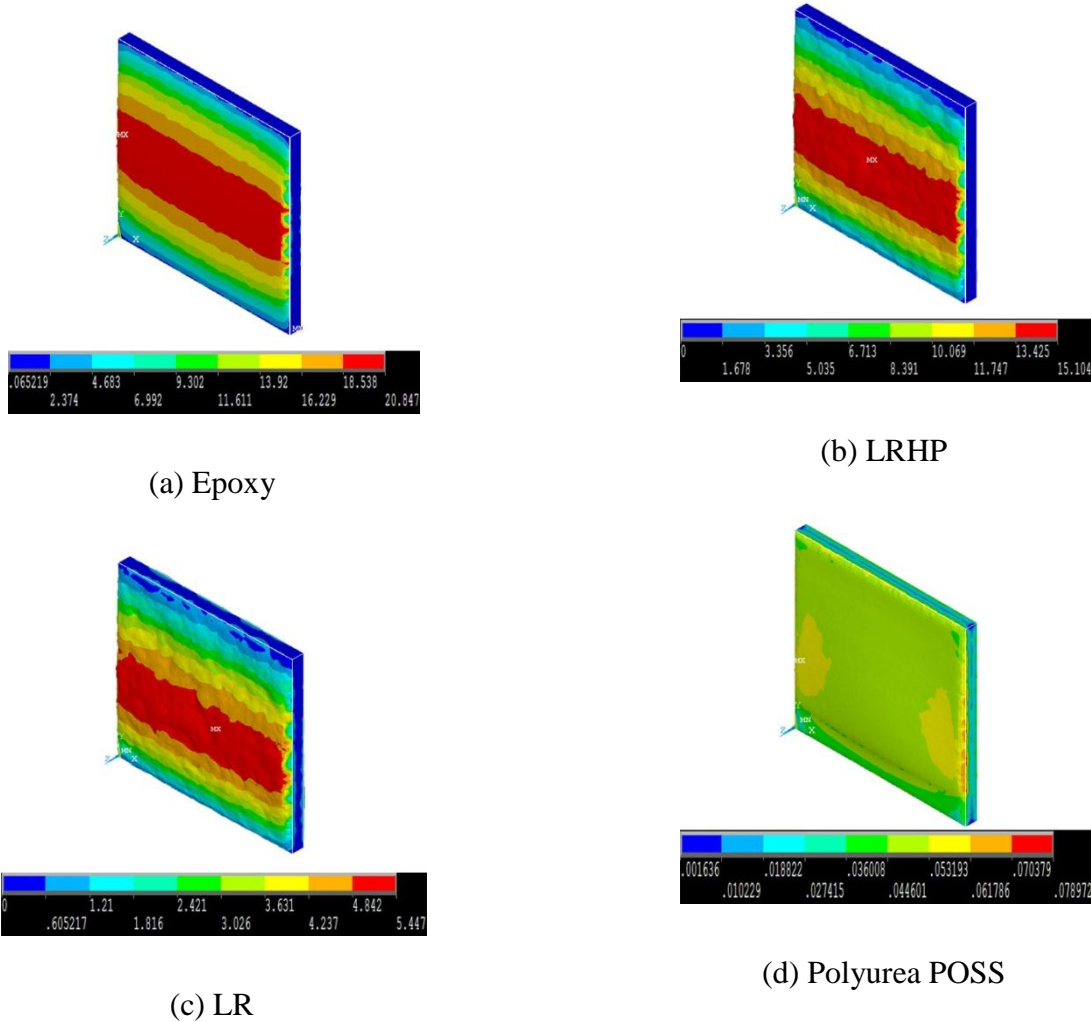


Figure17: Von Mises Strain Nodal Distribution in Masonry Coated Walls

The total mechanical von Mises stress/strains contour plots are shown in Figures 16 and 17. The results shown confirm that the polyurea POSS coated masonry walls performed the best in terms of mechanical stress and strain performance compared to the other polymeric blast-resistant coatings.

4. CONCLUSIONS

The blast-resistant material coatings have similar behavior in terms of maximum heat flux and stress/strains. The addition of POSS and graphene has been shown to reduce the HRR of polyurea. On the other hand, addition of graphene platelets to epoxy coatings has the opposite effect; increasing the HRR, maximum heat flux and maximum surface

temperatures. The simulations indicate that fire-retardant coatings, such as LRFCF and HP, are effective in reducing the peak HRR of an existing fire. LR performed the best in terms of maximum HRR and smoke density and visibility.

5. ACKNOWLEDGEMENTS

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